Synthesis Gas Conversion to Gasoline Range Hydrocarbons
over Medium Pore Zeolite Catalysts Containing 3d-Metals and Bimetallics

V. U. S. Rao, R. J. Gormley, H. W. Pennline, L. C. Schneider and R. Obermyer*

Pittsburgh Energy Technology Center
4800 Forbes Avenue
Pittsburgh, PA 15213

and

*Department of Physics
Pennsylvania State University
McKeesport, PA 15132

Introduction

There is much current interest in the conversion of synthesis gas to gasoline range hydro-
carbons using bifunctional zeolite catalysts (1,2). The medium pore (dia 6Å) zeolite
ZSM-5 in combination with Fe was shown to yield a high fraction of aromatics in the
product, resulting in a favorable octane number ($\approx$ 90). The transition metal (TM)
component catalyzed the hydrogenation of CO while the acid function of the zeolite led
to an aromatic product. Owing to the medium size pores of ZSM-5 there was a fairly
sharp cut-off, in the product distribution near the end of the gasoline range for the
aromatic fraction.

In order to explore further the role of the TM component and the acidity of the zeolite
on the product composition, experiments were performed in our laboratory on ZSM-5
impregnated with Fe and Fe-Co, and on Silicalite impregnated with Fe. Silicalite is a
molecular sieve form (3) of SiO_2.

A comparison of the crystallographic studies (4,5) on ZSM-5 and Silicalite, shows that
the two zeolites possess very similar crystal structures. While the Si/Al ratio in
ZSM-5 can be varied from 3 to ∞, Silicalite has essentially no Al. Hence, it appears
that Silicalite is the limiting form of ZSM-5 when the Al concentration is vanishingly
small. Owing to the lack of cations which can be exchanged with protons, Silicalite
has no acidity, while HZSM-5 is a highly acidic zeolite. Our investigations sought
to find the difference in selectivity for synthesis gas conversion by ZSM-5 (Fe) and
Silicalite (Fe) catalysts resulting from the above mentioned difference in acidity.

A further aim of the investigation was to investigate possible difference in selectivity
between ZSM-5 (Fe) and ZSM-5 (Fe-Co) catalysts, resulting from the different 3d-electron
concentration of the TM component. Magnetic studies (TMA) were performed to characterize
the TM component and particularly to detect the formation of bimetallic Fe-Co clusters.

Experimental

The zeolites were prepared using methods described in the literature (3,6). The metal
component was introduced by gradually adding the metal nitrate solution to the zeolite
until incipient wetness was reached. The impregnation with the metal nitrate solution
was carried out for an hour under vacuum in order to enable the nitrate solution to
enter the pores of the zeolite. The material is initially dried with constant stirring
over a boiling water bath, and further dried in air at 110° C for 12 hours. It is then
pelleted to yield tablets 3mm in diameter. In the case of the Silicalite based catalysts,
about 10% by weight of an amorphous silica such as Ludox AS-40 was added as a binder
before the pelletization step.

The catalysts were tested for synthesis gas conversion in both a fixed bed microreactor and a Berty (continuous flow stirred tank) reactor (7). The latter is shown in Figure 1. The catalyst pellets were loaded into the 2-inch diameter CFSTR chamber and retained by glass wool with a screen. Impeller speed was 1240 rpm. Excellent bed temperature control was obtained by a modification which involved the installation of a coil in the head of the reactor through which air could flow for faster heat removal.

A schematic diagram of the reactor system is shown in Figure 2. Synthesis gas with a H_2/CO-ratio of either 2/1 or 1/1 would pass through a carbon trap and enter the reactor. Liquid and solid hydrocarbon products are collected in a hot trap usually maintained at 150° C and in an ice trap. This series of traps are alternated and drained periodically. Product gases are metered and then flared.

The tablets of the zeolite impregnated with TM were reduced in flowing H_2 at 21 bar and 450° C for 24 hrs. They were then carbided with synthesis gas at 7 bar and 250° C for 24-48 hrs to yield the active catalyst. The gas phase product (C_1-C_4 hydrocarbons) was analyzed by gas chromatography. The liquid product was separated into paraffins, olefins, aromatics and oxygenates by column chromatography using FIA detection.

<div align="center">Results and Discussion</div>

(a) Influence of Zeolite Acidity:

The results obtained in the Berty reactor on the catalysts ZSM-5 (11.1 wt% Fe) and Silicalite (13.6 wt% Fe) are shown in Table 1. It is apparent that a high percentage of aromatics is obtained from the ZSM-5 (11.1% Fe) catalyst, while the product from the Silicalite (13.6% Fe) catalyst has a low aromatic fraction but much higher olefin and oxy-genate fractions. It is thus apparent that the acid function of ZSM-5 based catalyst is responsible for the conversion of the olefins and oxygenates to aromatics. The aromatic fraction imparts a high octane number to the product.

(b) High Olefin Yields from Silicalite Based Catalysts:

The interesting aspect of the product slates from the Silicalite based catalysts was the high percentage of olefins in both the gas and liquid phase products. When promoted with potassium, the Fe containing Silicalite catalyst yielded a large C_2-C_4 olefin fraction as seen in Table 2. The C_2-C_4 olefin fraction from Silicalite (7.8% Fe, 0.9% K) in a fixed bed microreactor is compared with that from a precipitated Fe-Mn catalyst of Kolbel et al (8), known for its very high olefin yield. It is seen that the olefin yields from the two catalysts are quite comparable. The Silicalite (7.8% Fe, 0.9% K) catalyst yields a much higher C_2-C_4 olefin/paraffin ratio than the precipitated Fe-Mn catalyst and hence is of potential commercial interest. The mechanism for the enhancement of olefin production on adding K as a promoter has been discussed by Dry et al. (9).

(c) Influence of Transition Metal Component on Product Composition:

The addition of cobalt to Fe containing ZSM-5 catalyst was found to result in a marked change in product composition as seen from the Berty reactor study results in Table 3. It is seen that the incorporation of cobalt into the catalyst results in (a) reduction in the wasteful shift conversion as seen from the decrease in CO_2 in the product (b) lowering of the aromatic fraction to about 10% of the C_5^+ fraction. However, the octane number remained at a relatively high value of 81, despite the decrease in the aromatic fraction. Hence, the impregnation of zeolites with bimetallic TM clusters provides a promising means of altering the extent of shift conversion and the composition of the liquid product. Changes in the aromatic fraction with TM component was an unex-pected result since aromatization is normally associated with the acidity of the zeolite. It is possible that some of the cobalt is attached to the Al sites in the zeolite, reducing its acidity. Further studies on this subject are necessary.

(d) Magnetic Studies:

The magnetic properties of TM impregnated zeolite catalysts have been investigated between 77K and 923K in applied fields up to 21 kOe. Samples of ZSM-5 (11.1% Fe), ZSM-5 (5.6% Fe, 4.5% Co) and Silicalite (13.6% Fe) were magnetically analyzed after each of the impregnation, reduction and carburization steps and after use as a catalyst.

The reduced samples of ZSM-5 (11.1% Fe) and Silicalite (13.6% Fe) indicate that Fe is in the metallic state with 86% and 85% reduction, respectively. Thermo-magnetic analysis (TMA) of carbided ZSM-5 (11.1% Fe), show it to be in the high Curie point form (10) of the Hagg carbide. TMA analysis reveals the used ZSM-5 (11.1% Fe) to be the hexagonal close packed (hcp) carbide form of Fe_2C, and the used Silicalite (13.6% Fe) to be the high Curie point form of the Hagg carbide.

The TMA of ZSM-5 (5.6% Fe, 4.5% Co) shows that the reduced, carbided, and spent samples have large magnetic moments (1.94, 2.04 and 2.61μ_B per TM atom respectively, at room temperature) and high Curie points (> 900° C), which cannot be accounted for on the basis of individual Fe and Co particles. The magnetic data indicate the composition to be that of a Fe-Co alloy (11). Hence, we conclude that the difference in selectivity between ZSM-5 (11.1% Fe) and ZSM-5 (5.6% Fe, 4.5% Co) catalysts can be attributed to the presence of bimetallic TM clusters in the latter, with consequent changes in the average number of 3d-electrons per TM atom.

(e) TM Cluster Size and Bifunctional Catalysis:

To determine TM particle size in the bifunctional catalysts CO adsorption studies were performed to determine the TM surface area. These studies showed that the TM clusters had an average diameter of 100-110 Å. Owing to the limitations connected with CO adsorption for estimating metal surface areas, the above may be considered to be approximate values of the TM cluster diameter. Hence, the majority of the TM clusters must reside outside of the pores of the zeolite. We believe that the bifunctional catalytic behavior of these catalysts results from high interparticle diffusivity relative to intracrystalline diffusivity (12).

                              Conclusions

Our experiments lead to the following conclusions:

(1) Zeolite acidity plays an important role in the formation of aromatics from synthesis gas by bifunctional catalysts as strikingly evidenced in a comparison of the product slates from ZSM-5 (11.1% Fe) and Silicalite (13.6% Fe).

(2) The transition metal component impregnated into the zeolite plays an important role in selectivity as seen from the liquid phase products from ZSM-5 (11.1% Fe) and ZSM-5 (5.6% Fe, 4.5% Co). In this context, zeolites containing bimetallic clusters are of special interest.

(3) Silicalite impregnated with Fe and promoted with K has an exceptionally high selectivity for the production of C_2-C_4 olefins from synthesis gas.

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Table 1. - Comparison of Products from ZSM-5 (11.1% Fe) and Silicalite (13.6% Fe) Catalysts with $H_2/CO=2$, and P≈21 bar.

Catalyst	ZSM-5 (11.1% Fe)	Silicalite (13.6% Fe)
Temperature, °C	300	280
CO Conversion, %	68.2	39.4
H_2 Conversion, %	38.7	16.5
Space Velocity (h^{-1})	1500	1350

Product Composition (%)

CO_2	52.0	51.1
H_2O	19.4	22.1
CH_n + oxygenates	28.6	26.9

Hydrocarbon and Oxygenate Composition (%)

CH_4	54.1	26.5
C_2H_4, C_2H_6	1.1, 15.0	2.5, 15.0
C_3H_6, C_3H_8	2.1, 6.3	10.8, 7.2
C_4H_8, C_4H_{10}	0.0, 4.5	4.8, 4.8
C_5+ and oxygenates	16.9	25.0

Composition of C_5+ and oxygenates (%)

Aromatics	72	4
Olefins	3	41
Saturates	24	33
Oxygenates	1	22
%Gasoline range (BP <204° C)	75	77
Research octane No.	96	36

Table 2. - Conversion of Synthesis Gas to Olefins in Fixed Bed Reactors, Using Silicalite (7.8% Fe, 0.9% K) Compared with That Using a Precipitated Fe-Mn Catalyst of Kolbel et al (8).

Catalyst	Silicalite (7.8% Fe, 0.9% K) (our)	Precip. Fe-Mn (Kolbel et al)
Pressure (bar)	21	14
Temperature (°C)	280	290
H_2/CO Ratio	0.9	0.8
Space Velocity (h^{-1})	1300	353
Product Composition (CH_n + Oxygenates) %		
CH_4	8.6	12.1
C_2H_4	8.2	7.6
C_2H_6	0.4	4.9
C_3H_6	19.3	17.3
C_3H_8	<0.2	2.1
C_4H_8	8.6	15.2
C_4H_{10}	<0.2	3.1
C_2-C_4 Olefins	36.1	40.1
C_2-C_4 Paraffins	<0.8	10.1
C_5+ and oxygenates	55.1	47.8
$\dfrac{C_2-C_4 \text{ Olefins}}{C_2-C_4 \text{ Paraffins}}$	>45.1	4.0

Table 3. — Product Compositions from the Catalysts ZSM-5 (11.1% Fe) and ZSM-5 (5.6% Fe, 4.5% Co), in a Berty Reactor, Showing the Influence of cobalt addition to the Catalyst. Process Condition: $H_2/CO = 2$, P = 21 Bar and GHSV = 1000 hr^{-1}

Catalyst	ZSM-5 (11.1% Fe)	ZSM-5 (5.6% Fe, 4.5% Co)
Temperature	300	280
CO Conversion, %	68.2	37.8
H_2 Conversion, %	38.7	41.3
Space Velocity	1500	1400
Product Composition (%)		
CO_2	52.0	9.8
H_2O	19.4	51.8
CH_n + Oxygenates	28.6	38.4
Hydrocarbon and Oxygenate Composition (%)		
C_1-C_4 hydrocarbons	83.1	74.3
C_5+ and Oxygenates	16.9	25.7
Composition of C_5+ and Oxygenates (%)		
Aromatics	72	10
Olefins	3	46
Saturates	24	37
Oxygenates	1	7
% Gasoline range (BP 204° C)	75	94
Research octane No.	96	81

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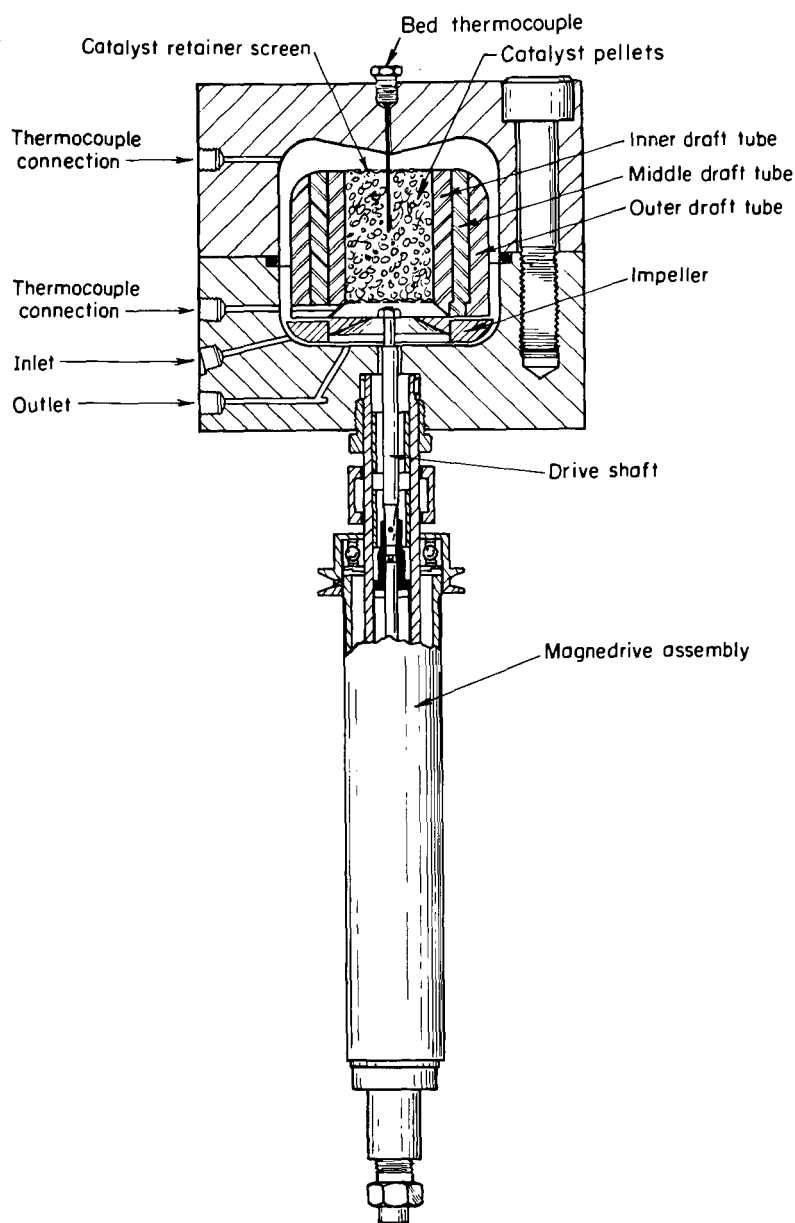
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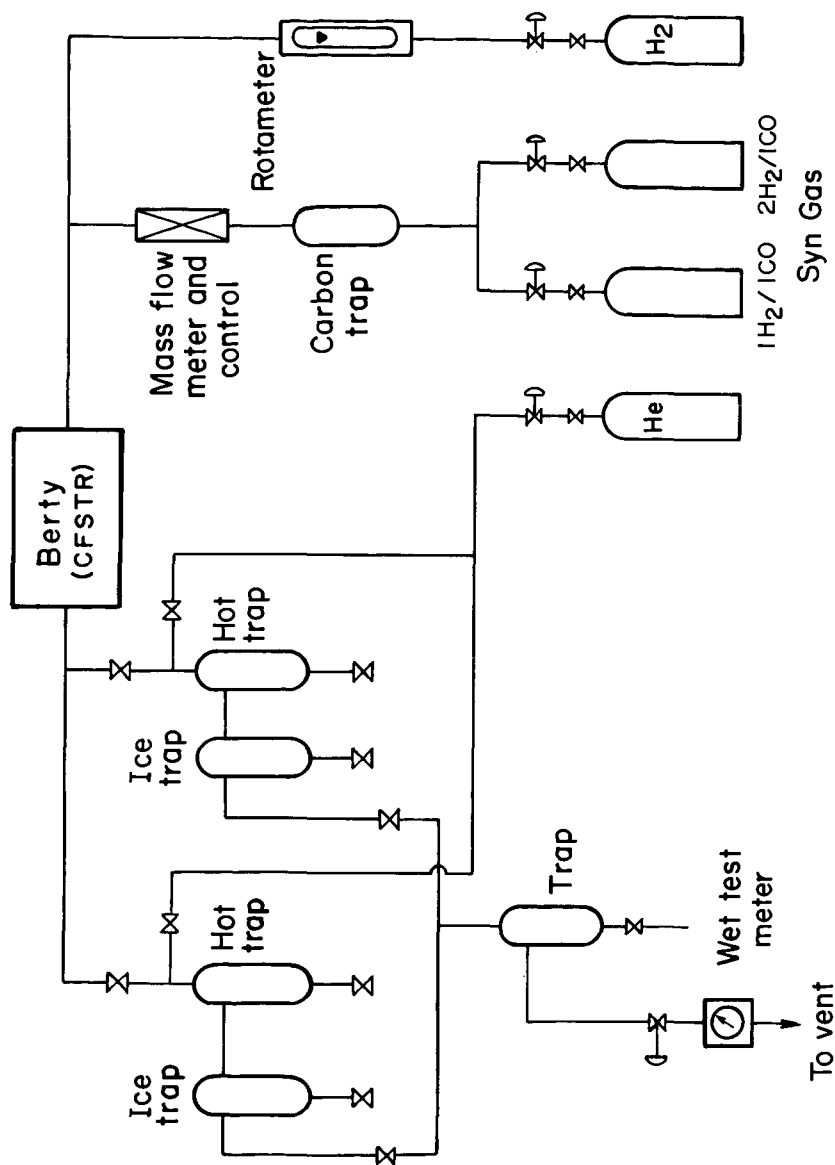
Figure 1. - Berty Reactor (CFSTR)

Figure 2. – Flow Diagram for Berty Reactor System